SDEP and SAME Lunch Discussions

TestAmerica

THE LEADER IN ENVIRONMENTAL TESTING

The Analysis of Polyfluorinated Alkyl Substances (PFAS) Including PFOS and PFOA

Karla Buechler – Corporate Technical Director

PFAS - Outline

Introduction to PFASs

What are PFASs?

Nomenclature/Chemistry

Sources, Timeline, Formation

Exposure, Toxicity and Risk

Regulatory Review

Analytical Best Practices

Analytical Methods review

Why so much variability?

How do we reduce variability?

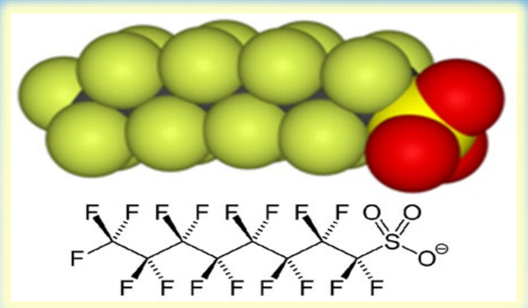
New DAI Capability

Future Concerns – TOP Assay

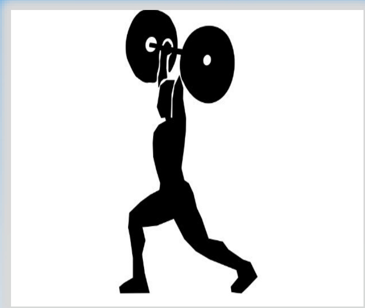
Capabilities and Questions?

Briefly - What are PFASs?

Class of synthetic compounds containing thousands of chemicals formed from **carbon** chains with **fluorine** attached to these chains.



The **C-F** bond is the shortest and the strongest bond in nature.



PFOS and PFOA are fully fluorinated and the most common perfluorinated chemicals (PFCs).

Persistent and resistant to degradation
Found in soil, air and groundwater..

Nomenclature

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PFAS – Broad term – completely and incompletely fluorinated

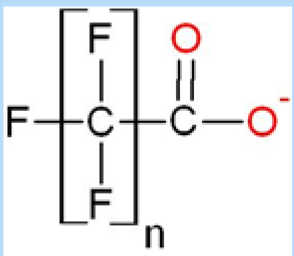
PFC – Subset of PFAS completely fluorinated compounds. PFOS and PFOA are PFCs (no hydrogen atoms)

PFAAs – Perfluoroalkyl acids – 2 classes PFCAs and PFSAs

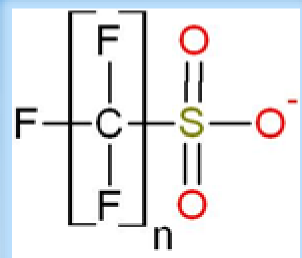
AFFF – Aqueous Film Forming Foam –mixture of PFCAs, PFSAs, and PFAS precursors

Fluorochemicals and telomers

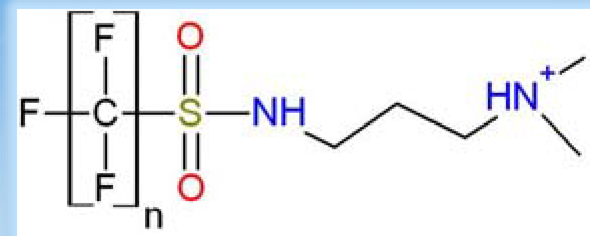
Chemical Structure
Why is it Important?



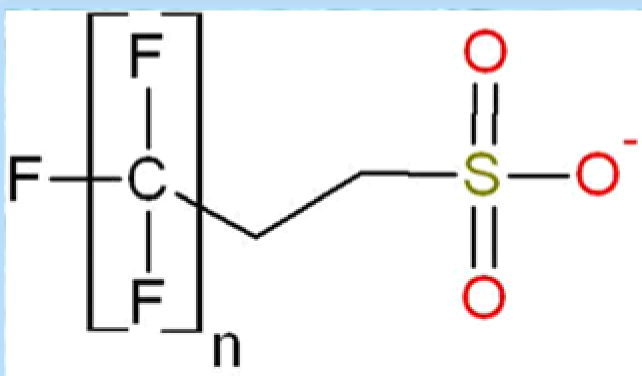
Perfluoroalkyl Carboxylate



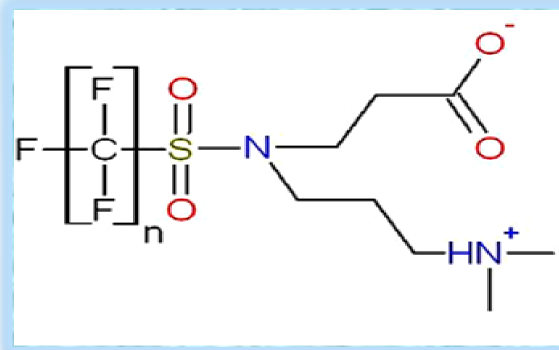
Perfluoroalkyl Sulfonate



Perfluoroalkyl Sulfonamido Amines



Fluorotelomer Sulfonates



Perfluoroalkyl Sulfonamido acetic acid amine

Primary Sources – Point or Direct

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- Released in large quantities from primary manufacturing facilities
- Secondary Manufacturing – incorporation of PFC raw materials into industrial and consumer products
- The use of AFFFs to fight fires is a direct pathway to the environment – (Connection to DoD)

Secondary Sources - Indirect

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- Commercial and consumer products have a finite lifetime.
  - Dispose to landfills
  - WWTP
  - Air emissions
- **Trace chemistry – transformation mostly degradation by-products (TOP Assay)**

PFAS – Historical Timeline

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When	What Happened
1950s	3M was first to produce PFOS and higher homologues
1969	AFFF was patented as a method for extinguishing liquid hydrocarbon fires and implemented by the DoD in 1969
1980s – 90s	**First LCMSMS instruments with ppm to ppb detection capabilities**
1990s	A handful of commercial labs developed propriety methods to meet client needs
2002	Global manufacturers began to replace LC PFCs with SC PFCs
2005	$235Mil class action lawsuit brought by citizens against DuPont over PFC contamination in the Ohio river
2000s	**LCMSMS technology advancements lead to ppt and ppq DLs.**
2008, 09	**EPA published Method 537 and Method 537 Version 1.1**
2011	EPA published Draft Procedure for Analysis of PFCA and PFSA in Sewage Sludge and Biosolids by HPLC/MS/MS
2012	UCMR3 was signed by the EPA administrator
2014	ASTM Published Method D7968-14 for PFC in Soil by LC/MS/MS
2015	ASTM Published Method D7979-15 for PFC in Water, Sludge, Influent, Effluent and WW by LC/MS/MS

PFAS Formation by ECF

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- **ECF Reaction: Process yields a mixture of B/L isomers**

(5 volts)

$$C_8H_{17}SO_2 + 34HF \rightarrow C_8F_{17}SO_2F + 17H_2 \text{ (POSF)}$$

- **Telomer Reaction: Process yields 100% linear isomers**

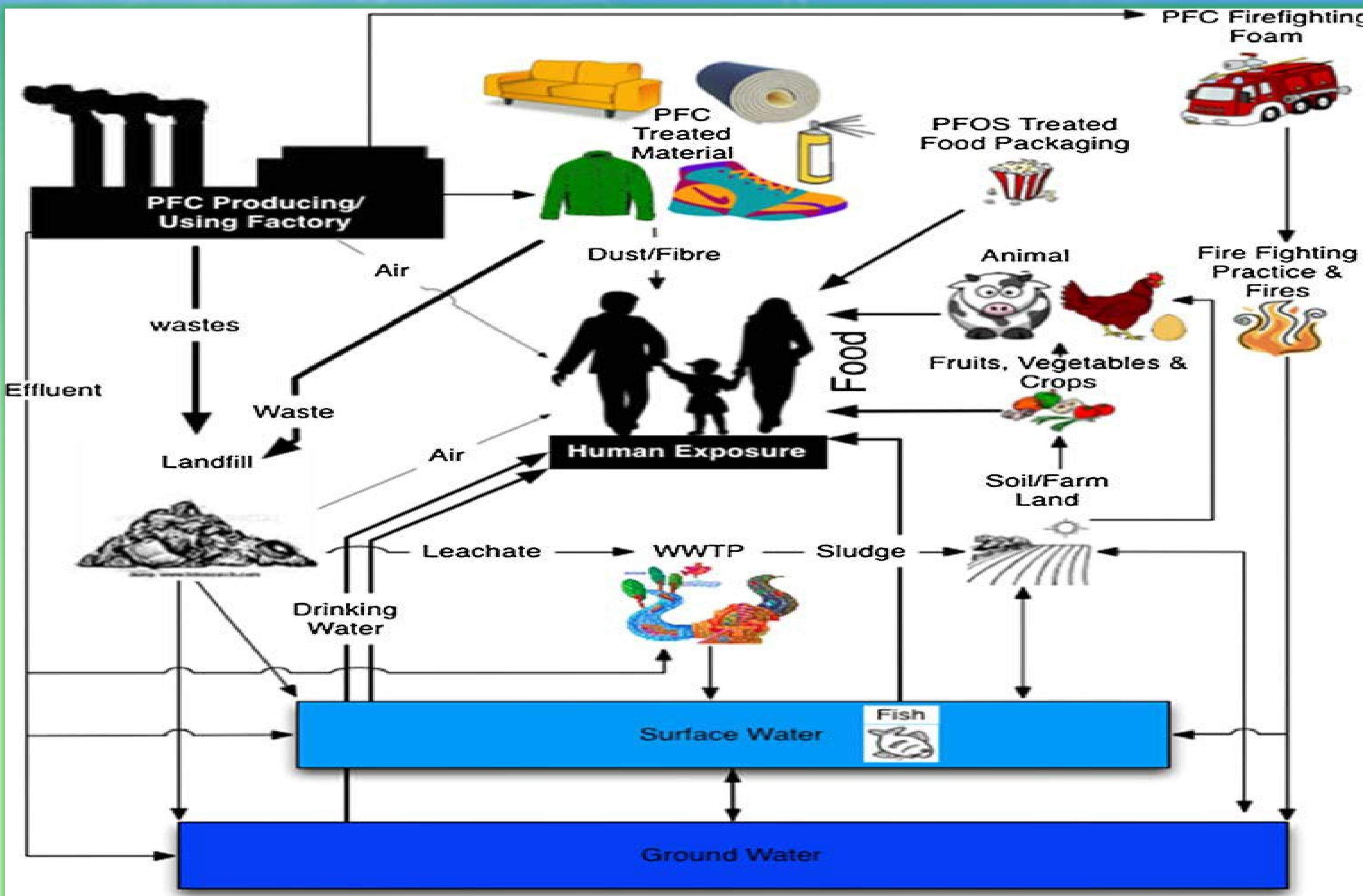
(Synthesis of building blocks leading to fluorotelomer alcohols)

(Telomer alcohols)

$$F(CF_2)_2I \xrightarrow{+\ CF_2{=}CF_2} F(CF_2)_nI \xrightarrow{+\ CH_2{=}CH_2} F(CF_2)_nCH_2CH_2I \longrightarrow F(CH_2)_nCH_2CH_2OH$$

Environmental Exposure Pathways

Oliaei, Environ Pollut Res. (2013): 1977-1992



Exposure, Toxicity and Risk

- Major source of non-occupational exposure to humans is from food and air (predominately fish consumption)
- Human and wildlife exposure can continue even though the chemicals are no longer in use, due to persistence.
- PFOS and PFOA have half-lives in humans ranging from 2 to 9 years, depending on the study.
- PFOA associated with liver, pancreatic, testicular, and mammary gland tumors in laboratory animals. PFOS causes liver and thyroid cancer in rats
- PFOA and PFOS are associated with cancers in humans. Pathways are being studied.

PFAS – Regulatory Timeline

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When	Who	What Happened
1980s	EU	Groundwater directive to prevent discharge of PFOS
2002	US EPA	Initiated voluntary phase out of PFOS
2002	3M	Discontinued making PFOS (7 other makers complied)
2006	US EPA	Announced 2010 (95%)/15(100%) PFOA Stewardship Program
2008	Canada	Regulated and prohibited PFOS imports to Canada
2009	UN	Stockholm Convention - adds PFOS to Annex B
2010	US EPA	2010 PFOA Stewardship program - must reduce PFOA use by 95%
2013	Canada	Use of AFFF with PFOS > 0.5ppm are prohibited
2013	DuPont	Makes a statement that it does not make, buy or use PFOS
2015	US EPA	Must 100% eliminate the use of PFOA by December 31,2015
May 2016	US EPA	PFOS and PFOA life time health limits reduced to 70 ppt each or the total if both are present.

Input from Dr. Jimmy Seow Dept. of Environment and Conservation Western Australia.

What's Up in New Jersey?

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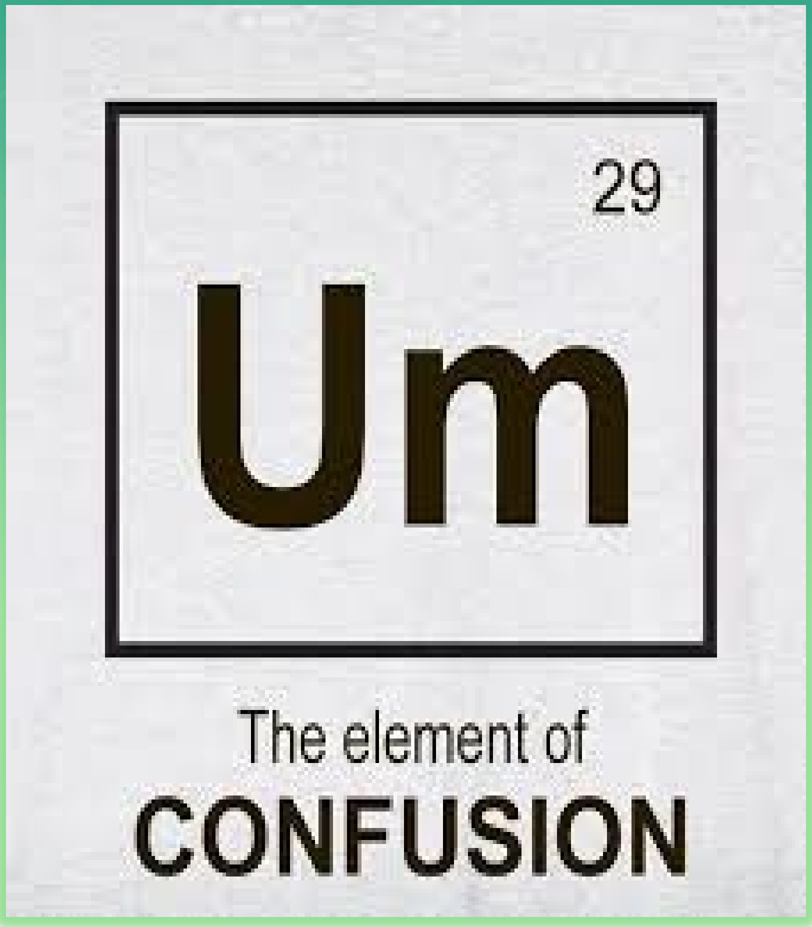
State	PFOA ppt	PFOS ppt	Comments	Source	Year
Alabama	400	200		EPA	2009
Alaska	400	400		ADEC	2016
California	400	200		OEHHA	2010
Georgia	400	200		EPD	2009
Illinois	400	200			
Maine	60	100		ME DEP	2014
Michigan	42	11		MI DEQ	2013
Minnesota	300	300	700 PFBA	MDH	2009
New Jersey*	**14**	**14**		**NJDEP**	**2016**
North Carolina	1000	NA		NCSAB	2009
Ohio	400	200		EPA	2009
Oregon	24000	300000	PFHpA, PFNA, PFOSA		
Pennsylvania	TBD	TBD		PA DEP	2015
Texas	100	100	PCLs for 16 PFCs		2013
Vermont	20	TBD		VT DOH	2016
Washington	NA	TBD	Listed PFOS as PBT		
West Virginia	400	200		EPA	2009

PFAS Analytical Methods- Best Practices

- Manufacturer's methods were adopted by the environmental industry – SW-846 Method 8321
- EPA expanded manufacturer's method for drinking water- Method 537
- EPA expanded Method 537 for biosolids and sewage matrices – Draft EPA Method
- ASTM published D7968-14 for soils
- ASTM published D7979-15 for a wide variety of aqueous matrices



Why so much method variability? (May 2016)

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- **Inconsistent quantitation of branched and linear isomers**
- Absence of multi-lab validated methods
- Limited certification programs
- Differences in extraction efficiencies – analyte sorbent dependent
- External, internal and isotope dilution quantitation schemes
- **Lack of proven commercially available PT samples**
- Use of isotopically labeled extraction surrogates
- Lack of commercially available standard materials and true second sources
- Target analyte losses during filtration
- Absence of demonstrated cleanup techniques for complex matrices
- **Wide variety of container types and holding times**

Show Branched and Linear error in PFOS and PFOA

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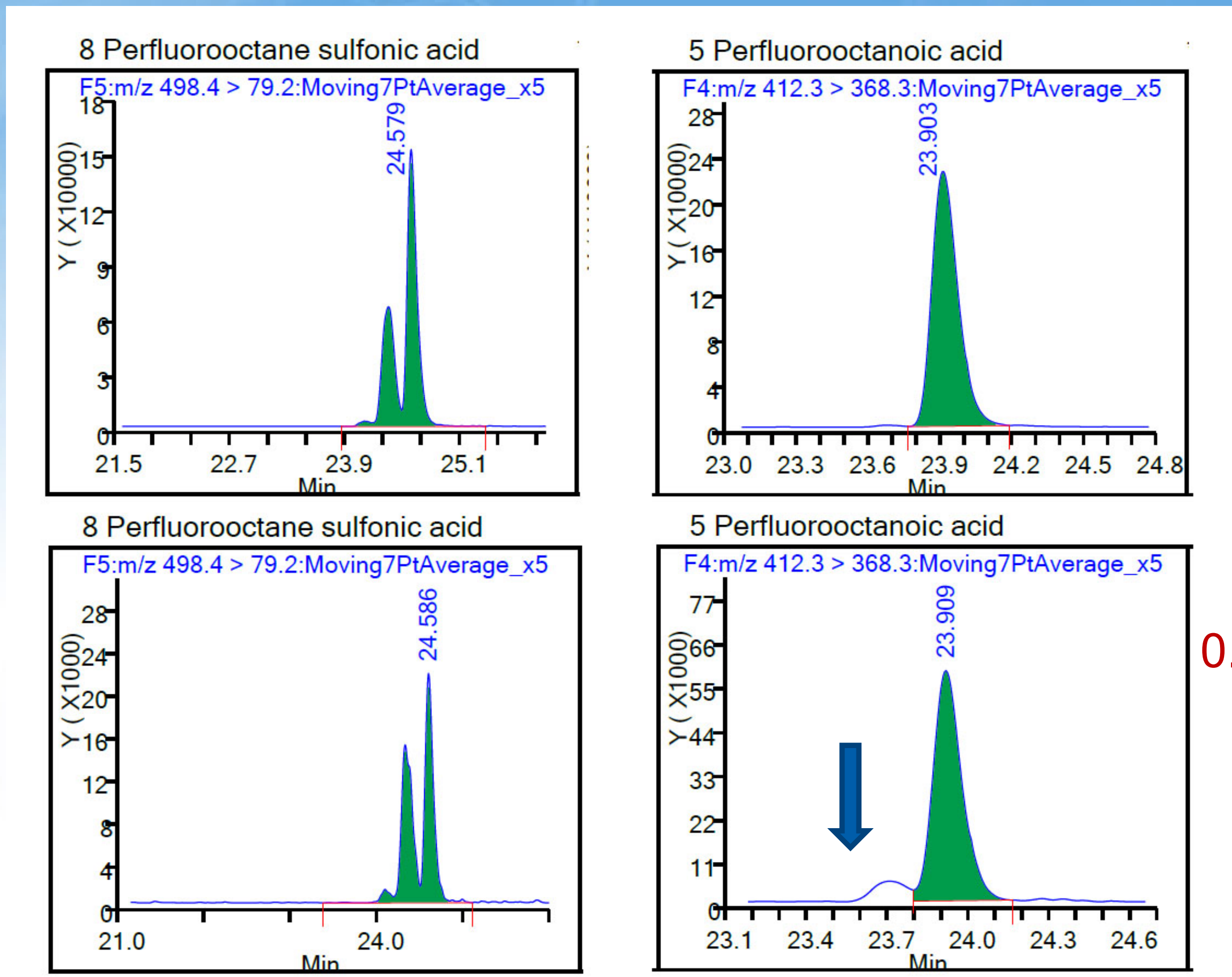
Standard

Sample



0.99 vs 1.20 ng/ml

PT variability May 2016

- What is the pH?
- Is there headspace in an aqueous container?
- Is the spiking standard stored in methanol?
- What kind of containers and lids are used?
- Does the spiking container have branched and linear isomers?
- Was water PFAS free?
- Were the spiking levels verified by third party?
- Were the acceptance levels verified by third party?

Study Results - NMI PT

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- 24 labs submitted results – 9 Passed
- TestAmerica passed water, soil and fish tissue samples

Sample	Analyte	Sac Lab	Expected
Water A	PFOA	7.91	7.90
	PFOS	3.23	3.00
Water B	PFOA	9.01	10.8
	PFOS	6.81	6.50
Soil A	PFOA	7.00	5.83
	PFOS	290	262
Soil B	PFOA	14.2	12.0
	PFOS	23.5	22.0
Fish A	PFOA	ND	ND
	PFOS	19.9	20.6
Fish B	PFOA	51.4	50.5
	PFOS	49.2	53.7

Sample Collection and Holding Time Studies

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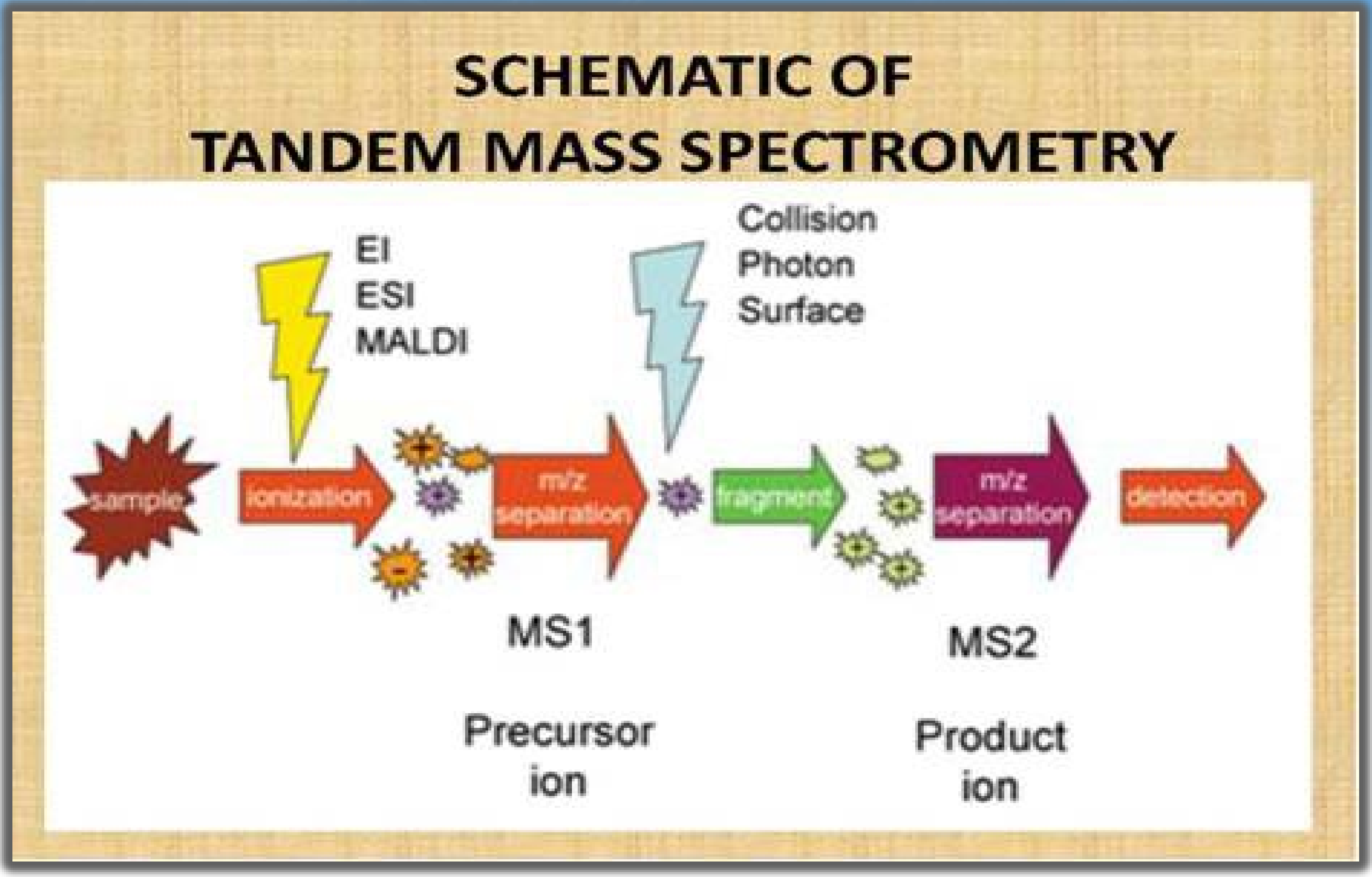
"Confusion and clutter are the failure of design, not the attributes of information."

- Samples should be collected in HDPE bottles fitted with unlined (no Teflon) polyethylene screw caps.
- In addition, the sampler should avoid contact with fluoropolymers, aluminum foil, and food wrappers.
- Samples should not be field filtered.
- Samples must be shipped chilled
- Limited HT studies

How can we mitigate analytical variability?

- Apply tandem mass spectrometry technology
- Implement an isotope dilution quantitation scheme
- Compensate for losses with matrix recovery correction
- Share our knowledge
- Invest resources in multi-lab validation

LC/MS/MS – Electrospray Ionization



Advantages of Isotope Dilution Quantitation

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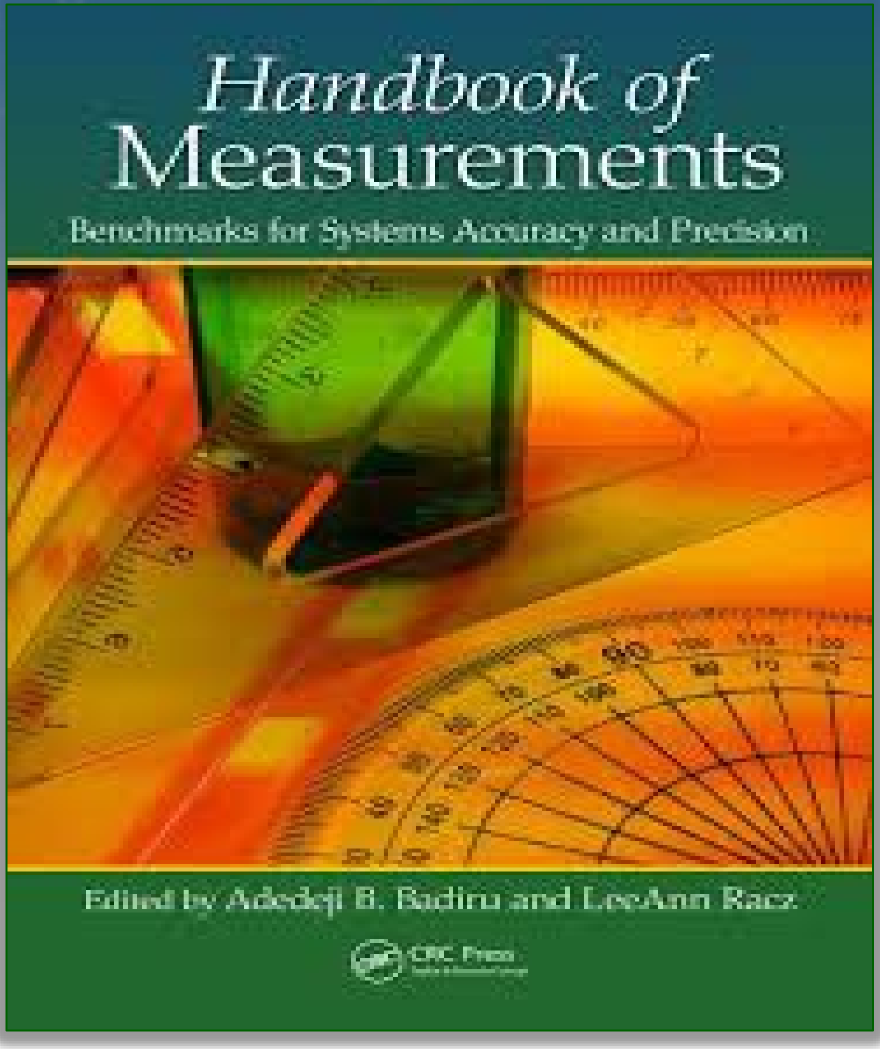
- Most accurate and precise calibration method available
- Partial loss of analyte during preparation is compensated for since chemical interferences are not an issue
- Allows for matrix recovery correction – what affects the native analyte will equally affect the isotope
- Correction for signal drift
- Improved qualitative identification – RT shifts



Compound Name	Abbr.	CAS #	Method 537	Aqueous (ng/L)		Soil (ug/Kg)	
Perfluoroalkylcarboxylic acids (PFCAs)				RL	MDL	RL	MDL
Perfluoro-n-butanoic acid	PFBA	375-22-4		2.00	0.458	0.200	0.0650
Perfluoro-n-pentanoic acid	PFPeA	2706-90-3		2.00	0.989	0.200	0.1310
Perfluoro-n-hexanoic acid	PFHxA	307-24-4	Y	2.00	0.786	0.200	0.0710
Perfluoro-n-heptanoic acid	PFHpA	375-85-9	Y	2.00	0.802	0.200	0.0880
Perfluoro-n-octanoic acid	PFOA	335-67-1	Y	2.00	0.748	0.200	0.102
Perfluoro-n-nonanoic acid	PFNA	375-95-1	Y	2.00	0.654	0.200	0.0830
Perfluoro-n-decanoic acid	PFDA	335-76-2	Y	2.00	0.440	0.200	0.0570
Perfluoro-n-undecanoic acid	PFUnA	2058-94-8	Y	2.00	0.748	0.200	0.106
Perfluoro-n-dodecanoic acid	PFDoA	307-55-1	Y	2.00	0.584	0.200	0.121
Perfluoro-n-tridecanoic acid	PFTrDA	72629-94-8	Y	2.00	0.551	0.200	0.0920
Perfluoro-n-tetradecanoic acid	PFTeDA	376-06-7	Y	2.00	0.199	0.200	0.0580
Perfluoro-n-hexadecanoic acid	PFHxDA	67905-19-5		2.00	0.123	0.200	0.0520
Perfluoro-n-octandecanoic acid	PFODA	16517-11-6		2.00	0.672	0.200	0.100
Perfluorinated sulfonic acids (PFSAs)							
Perfluoro-1-butanesulfonic acid	PFBS	375-73-5	Y	2.00	0.918	0.200	0.103
Perfluoro-1-hexanesulfonic acid	PFHxS	355-46-4	Y	2.00	0.870	0.200	0.118
Perfluoro-1-heptanesulfonic acid	PFHpS	375-92-8		2.00	0.713	0.200	0.118
Perfluoro-1-octanesulfonic acid	PFOS	1763-23-1	Y	2.00	1.28	0.200	0.126
Perfluoro-1-decanesulfonic acid	PFDS	335-77-3		2.00	1.21	0.200	0.0720
Perfluorinated sulfonamides (FOSA)							
N-ethylperfluoro-1-octanesulfonamide	EtFOSA	4151-50-2		100	13.0	20.0	2.53
N-methylperfluoro-1-octansulfonamide	MeFOSA	31506-32-8		100	22.4	20.0	3.36
Perfluorinated sulfonamidoacetic acids (FOSAA)							
N-ethylperfluoro-1-octanesulfonamidoacetic acid	EtFOSAA	2991-50-6	Y	20.0	5.02	2.00	0.390
N-methylperfluoro-1-octanesulfonamidoacetic acid	MeFOSAA	2355-31-9	Y	20.0	5.64	2.00	1.30
Perfluoroalkylsulfonamidoethanols (PFOSEs)							
2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol	Et-FOSE (N-Et-FOSE)	1691-99-2		40.0	7.50	4.00	0.750
2-(N-methylperfluoro-1-octanesulfonamido)-ethanol	Me-FOSE (N-Me-FOSE)	24448-09-7		40.0	7.30	4.00	0.750
Fluorotelomer sulfonates (FTS)							
1H,1H,2H,2H-perfluorooctane sulfonate (6:2)	6:2 FTS	27619-97-2		20.0	3.82	2.00	0.390
1H,1H,2H,2H-perfluorodecane sulfonate (8:2)	8:2 FTS	39108-34-4		20.0	4.04	2.00	0.680

Method 537M – DAI

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- **What is it?**
  - Dilute a water sample with methanol and inject a large volume onto a modified UPLC
- **What are the advantages?**
  - Simplicity – reduced sample manipulation
  - Reduced sample volume (5 mls)
  - Speed, reduced TAT
  - Increased capacity
  - Reduced risk of laboratory background artifacts

Future Concerns

- The TOP assay and PIGE demonstrate the mass balance is not closed
- Analyte lists are growing for discrete methods, may lead to forensics.
- LC PFASs are being replaced by SC PFASs and little is know about the toxicity
- On-going method confusion must be improved
- On-going data variability must be improved

What is the TOP Assay?

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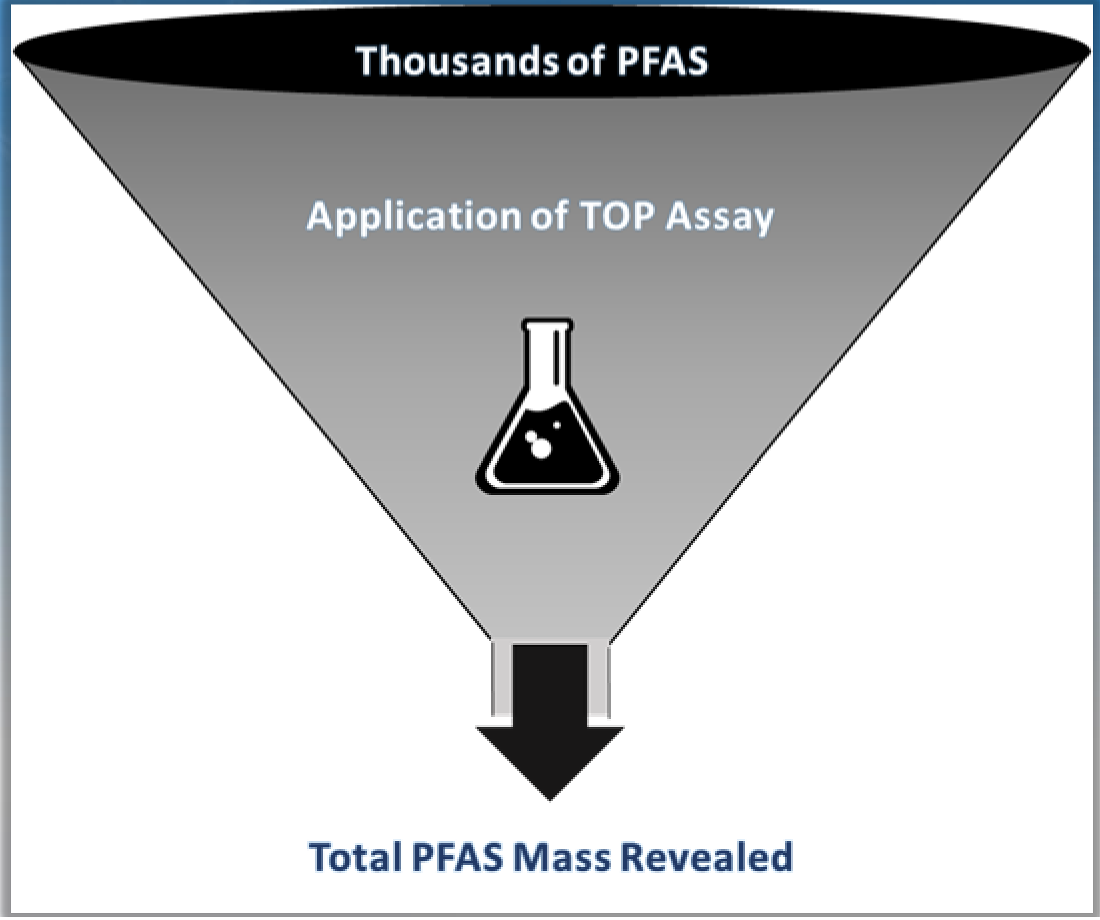
- A new PFAS sample preparation technique
- Pretty simple chemistry
- Used in conjunction with 537M (Not 537) – combines pre and post oxidation results
- Indicates presence of unidentified PFAS in water, sediment and soil



Houtz, Erika, and David L. Sedlak. 2012. Oxidative conversion as a means of detecting precursors to perfluoroalkyl acids in urban runoff. *Environmental Science and Technology* 46: 9342-9349.

Image provided by Arcadis 2016

TOP – How Does it Work?

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PFAS Precursors + 85°C OH• OH• OH• = PFOA + other PFCAs

=

What Do the Results Mean?

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TOP Assay measures total PFCA

Precursor	Pre - TOP	Post - TOP	% Recovery
FOSA	32.68	ND	0%
MeFOSAA	19.38	ND	0%
EtFOSAA	18.83	ND	0%
6:2 FTS	31.69	ND	0%
8:2 FTS	26.37	ND	0%
PFCA	**Pre – TOP**	**Post - TOP**	**Total**
PFBA	24.94	27.16	109%
PFPeA	23.38	28.55	122%
PFHxA	26.49	34.87	132%
PFHpA	23.10	25.14	109%
PFOA	23.72	58.71	248%
	Total 122	Total 174	

TestAmerica Capabilities

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- TestAmerica Sacramento is EPA approved for Method 537 in drinking water
- Sacramento and Denver both are NELAP and DoD ELAP approved for Method 537M.
- 7 LCMSMS instruments capable of PFAS testing
- Sacramento has successfully implemented the TOP Assay

SDEP and SAME Lunch Discussions

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Thank you for attending

The Analysis of Polyfluorinated Alkyl Substances (PFAS) Including PFOS and PFOA

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